Ground State of Systems of Three Particles with Coulomb Interaction*

W. Kolos,† C. C. J. Roothaan, and R. A. Sack‡

Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago 37, Illinois

FOR any system of particles with purely radial interaction, in particular with Coulomb interaction, the wave functions for states with zero rotational quantum number depend only on the geometric configuration of the system. Numerical solutions for the eigenvalues and eigenfunctions of the nonrelativistic Schrödinger equation are known for a number of three-particle systems. The mathematical treatments have hitherto been based on the assumption that one or two of the particles have considerably bigger masses than the others and, in first approximation, can be considered as infinitely heavy; the effect of finite masses is then treated as a perturbation.

Systems with one heavy mass are represented by the helium atom and its isoelectronic series. The most accurate results have been obtained by applying variational methods to wave functions of the type

$$\psi = \text{const} \exp(-\alpha r_1 - \alpha r_2) P(r_1, r_2, r_{12}), \quad (1)$$

where P represents a polynomial in the interparticle distances or any equivalent polynomial expansion. This method was introduced by Hylleraas[1] and has been used by a large number of workers, culminating in the recent work by Pekeris.[2,3]

Systems with two heavy particles are usually treated on the basis of the Born-Oppenheimer approximation in which the Schrödinger equation is solved for the light particle only, the internuclear distance appearing as a parameter; the potential energy function thus obtained is substituted in a second Schrödinger equation for the motion of the heavy particles. The properties of the hydrogen molecular ion H_2^+ have been extensively investigated on this basis.[4-6]

Neither approach mentioned can serve as a satisfactory starting point when the masses of all the three particles are of the same order of magnitude, as is the case in the μ-mesonic molecules $p\mu p$, $d\mu d$, and $p\mu d$ and the positronium ion $e^+e^-e^-$. To unify the treatment for the S states of all possible nonrelativistic three-particle

systems, the writers have applied the variational procedure to a generalization of (1): the wave functions are chosen of the form

$$\psi = \text{const} \exp(-\alpha_{12} r_{12} - \alpha_{23} r_{23} - \alpha_{31} r_{31}) P(r_{12}, r_{13}, r_{23}), \quad (2)$$

where all the exponents α as well as the terms in the polynomial P can be chosen freely. The scheme is of greater generality than those used previously, as none of the masses need be assumed to be infinite. The computations were carried out on the Remington Rand Univac Scientific 1103A computer at Wright-Patterson Air Force Base, Ohio. The energies as well as the most important geometric averages have been calculated for a number of systems.

It was found that, with the single-precision arithmetic (eight significant figures) employed, wave functions of the type (2) yielded best results with from 50 to 60 terms. With longer polynomials, increased rounding-off errors nullify any theoretical improvement in the approximation of the true wave function by the expression (2). On the other hand, the flexibility in the choice of the exponential parameters α significantly reduces the number of terms required to achieve a prescribed accuracy. For a given ratio of the α's, the program automatically optimizes their absolute values (the scale factor); the best ratios are found by trial and error.

Since the calculations are not yet complete, a detailed description of both method and results will be presented in a later publication. The essential results obtained to date on symmetric systems are shown in Table I. For He, the results agree with the more detailed calculations of Pekeris to seven figures in the energy E and (for $M_3 = \infty$) to six in the expectation values of the dimensions. For the positronium ion $e^+e^-e^-$, the binding energy computed was 0.326 ev; the large size of this system is remarkable.

The approach of this paper proves increasingly unsatisfactory as two of the particles become very much heavier than the third. Thus, for $p\mu p$ a lower ground-state energy was found than that of Cohen, Judd, and Riddell,[7] who used the Born-Oppenheimer approximation, but already for $d\mu d$ the result is poorer. In the limit of H_2^+ the energy, which should correspond to the lowest vibrational level,[5] falls nearer the first excited level. The reason for this poor agreement is that for a

† Permanent (and present) address: Institute of Physics, Polish Academy of Sciences, 69 Hoza, Warsaw, Poland.
‡ Permanent address: British Rayon Research Association, Wythenshawe, Manchester 22, England.

[1] E. A. Hylleraas, Z. Physik 54, 347 (1929).
[2] C. L. Pekeris, Phys. Rev. 112, 1649 (1958).
[3] C. L. Pekeris, Phys. Rev. 115, 1217 (1959).
[4] E. Teller, Z. Physik 61, 458 (1930).
[5] V. A. Johnson, Phys. Rev. 60, 373 (1941).
[6] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London A246, 215 (1953).
[7] S. Cohen, D. J. Judd, and R. J. Riddell, Phys. Rev. 110, 1471 L (1958).

TABLE I. Ground-state energies E and expectation values of several symmetric three-particle systems.

System	He	He	$e^+e^-e^-$	$p\mu p$	$d\mu d$	H_2^+
$M_1=M_2$	1	1	1	1836.12	3671.42	1836.12
M_3	∞	7296.19	1	206.8	206.8	1
$e_1=e_2$	-1	-1	-1	1	1	1
e_3	2	2	1	-1	-1	-1
$\alpha_{13}=\alpha_{23}$	1.9	1.9	0.3737	0.738	0.855	0.798
α_{12}	0.22	0.22	0	0	0	0.228
n^a	60	50	50	32	32	32
$-E^b$	2.9037237	2.9033037	0.2619956	2778 ev	2981 ev	0.58305
$-E^b$ (from other sources)	2.903724376^d	2.90330464^d		2771 ev^e	2986 ev^e	0.59715^f
$\langle r_{13}\rangle^c$	0.929472	0.929604	5.506			
$\langle r_{13}^2\rangle^c$	1.193477	1.19380	48.75			
$\langle r_{12}\rangle^c$	1.422069	1.42224	8.580			
$\langle r_{12}^2\rangle^c$	2.516430	2.51700	93.94			

a Number of terms in the wave function.
b In atomic units (1 a.u. =27.21 ev), except for $p\mu p$ and $d\mu d$.
c In Bohr radii (1 a.u. =0.529 A).
d See reference 3.
e See reference 7.
f See reference 5.

small zero-point vibration the wave function as function of r_{12} has a sharp peak which can be well approximated by (2) only with a large number of terms. An alternative scheme, which can accommodate longer expansions with little increase in the rounding off errors, is being developed.

ACKNOWLEDGMENTS

Self-Consistent Field Theory for Open Shells of Electronic Systems*

C. C. J. ROOTHAAN

Laboratory for Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago 37, Illinois

1. REVIEW OF THE CLOSED-SHELL THEORY

IT is well known that the Hartree-Fock equation for a closed-shell ground state of an electronic system can be derived from the variational principle.[1,2] The wave function is put forward as an antisymmetrized product of one-electron functions or orbitals φ_i, each orbital being doubly occupied:

$$\Phi = (\varphi_1\alpha)(\varphi_1\beta)\cdots(\varphi_n\alpha)(\varphi_n\beta)$$
$$= [(2n)!]^{\frac{1}{2}}(\varphi_1\alpha)^{[1}(\varphi_1\beta)^2\cdots(\varphi_n\alpha)^{2n-1}(\varphi_n\beta)^{2n]}$$

$$= [(2n)!]^{-\frac{1}{2}}\begin{vmatrix} (\varphi_1\alpha)^1 & (\varphi_1\beta)^1 & \cdots & (\varphi_n\alpha)^1 & (\varphi_n\beta)^1 \\ (\varphi_1\alpha)^2 & (\varphi_1\beta)^2 & \cdots & (\varphi_n\alpha)^2 & (\varphi_n\beta)^2 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ (\varphi_1\alpha)^{2n-1} & (\varphi_1\beta)^{2n-1} & \cdots & (\varphi_n\alpha)^{2n-1} & (\varphi_n\beta)^{2n-1} \\ (\varphi_1\alpha)^{2n} & (\varphi_1\beta)^{2n} & \cdots & (\varphi_n\alpha)^{2n} & (\varphi_n\beta)^{2n} \end{vmatrix}. \tag{1}$$

1 D. R. Hartree, Repts. Progr. Phys. 11, 113 (1948); *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).
2 C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951). The notation and terminology introduced in that paper are adhered to in the present paper.